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MOLECULAR MECHANISMS OF CLAYS IN SUSPENSION

BY

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Louis Rolland Berner

ENTITLED Molecular Mechanisms of Clays in Suspension

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

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A C K N O W L E D G E M E N T

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TABLE OF CONTENTS

INTRODUCTION. 1

HISTORICAL 2

THEORETICAL. 4

METHODS OF STUDY. 7

EXPERIMENTAL METHODS. 8

EXPERIMENTAL RESULTS. 11

SUMMARY AND CONCLUSIONS. 13

BIBLIOGRAPHY. 15

MOLECULAR MECHANISMS OF CLAYS IN SUSPENSION.

I

INTRODUCTION.

With the importance of colloidal chemistry becoming more pronounced every day, and clay being one of the socalled colloidal systems, the action of acids, bases and salts upon this material has become an important problem to the investigating chemist. The purpose of this paper shall be to tell how, by observation and measurement, a study was made of the suspendening tendencies of clays as affected by certain reagents. It will tell, also, of the attempts that were made to actually measure by titration the adsorbing ability of clays, and how this property was altered by the introduction of other substances.

DEFINITION OF CLAY.

A clay may be defined as a mixture of minerals most of which are hydrous silicates of aluminum, iron, the alkalies, and the alkaline earths; the most common one being hydrated aluminum silicate, Al_2O_3, $2SiO_2$, $2H_2O$. Some quartz, mica and feldspar may be present. Coatings of colloidal material consisting of silicates, silicic acids and hydroxides of aluminum, iron, and manganese usually envelope the grains of the constituent minerals and it it to these that the scientist ascribes the characteristic properties of a clay.

II

HISTORICAL.

That clays contained colloidal substances was known by Schloessing, (1), as early as 1874 and it is the opinion of Ashley, (2), Rohland, (3), and Gedroiz, (4), who worked in the later years, that the colloids of soil are due to hydrated gelatinous aluminum silicates, gelatinous silicic acid, hydrated ferric oxides and organic colloids. Usually colloids are thought to give to clay the following properties:-

Plasticity,
Granulation or deflocculation,
Absorption and adsorption,
Viscosity.

PLASTICITY.

The plasticity of a clay is perhaps its most important property, at least it is so from the standpoint of its practical use.

It is the opinion of Grout, (5), that colloids are not responsible for the phenomenon of plasticity, but that there is a molecular attraction between particles of clay and the particles of water. Colloidal effects, he claims, must come from organic colloids, and that inorganic colloids reduce rather than increase plasticity.

On the other hand Schloswig, (6), supposed that the properties of a clay were due to its colloidal content and this was later advocated by Rohland, (7), and made quite conclusive by A. S. Cushman's (8), recent work on the binding power of road making materials.

Le Chatelier, (9), attributes plasticity to the presence of very small lamellae, and claims that a plastic substance may even be made up from such lamellea. Wiley, (10), and Grimsley, (11), with slight modifications, have similar views.

GRANULATION AND FLOCCULATION.

Granulation and flocculation are sometimes looked on as the formation of compound particles. These formations take place when a clay suspension is flocculated and settled by additions of electrolytes. The electrolytes may be the neutral salts of H_2SO_4, HCl and HNO_3 as well as the acids themselves.

Ashley, (12), has done a considerable amount of work on this phenomena.

ADSORPTION AND ABSORPTION.

It was at first thought that these phenomena would be of great importance in the measurement of colloidal content in clays, but up to this time, varying results and the adoption of different standards and methods of measuring adsorption have led to a number of disagreements.

Ashley and Bleininger, (13), have made the most recent and complete study of this phenomena with dyes, acids, alkalies, and salts.

VISCOSITY.

Inasmuch as colloids usually require water for their existence, it is natural to suppose that the extent of colloidal content and the methods of making it the most effective, would have a direct bearing on the viscosity of clay in solution. This property has been investigated quite thoroughly by A. V. Bleininger, (13), and he finds that the viscosity of certain clay water systems may be surprisingly changed by small additions of Na_2CO_3 and Na_2SiO_3.

III.

THEORETICAL.

As has been stated before, the action of acids, bases, and salts upon clay solutions has been of extreme importance, and it is along these lines that investigations for this paper have been confined.

Bleininger, (13) states that "the deflocculating effect of alkalies may be visually observed by change in appearance of suspension, the holding up of cloudy masses of the material and also by the determination of the viscosity of the clay-water system," Deflocculation, he believes, corresponds to decreasing viscosity and that the maximum stage coincides with minimum viscosity.

By comparing a drop of alkaline suspension under the microscope with a drop of the ordinary water slip, Bleininger found that the alkaline solution contained a far greater number of particles showing the Brownian movement. The evidence leads to the thought that the alkali increases the dispersion of the clay particles. Neutralization of the alkaline suspension, and making slightly acid, causes a coagulation of the suspended particles and their subsequent precipitation, leaving the supernatant liquid clear. "The Brownian movement of particles", says Bleininger, "will have diminished greatly because of their sizes, and claims that the prompt settling of the granular particles, brought about by the decreased viscosity of the system, is explained by Stoke's law: $v = \frac{2r^2g}{9k}(d-d_1)$, where

v = the velocity of settling,

r = radius of particles,

k = viscosity,

d = density of particles

d_1 = density of fluid

g = gravity constant

If dispersion is the principal function involved, it is to be assumed that the small grains of clay already present should be still further subdivided into microscopic particles resulting in an emulsoid-like substance. Such a material has been separated (15), by filtering an alkaline clay suspension. The emulsoid must play an important part in the suspension, tending to prevent further decrease in viscosity and to hold up fine particles which might tend to settle.

Bleininger, (13) believes the theory is generally accepted that the liquifing action of alkaline salts, sodium carbonate, and sodium silicate upon clay is due to the action of OH' ions. Both salts are strongly hydrolyzed, containing an excess of hydroxyl ions according to the state of equilibrium. Typically, sodium carbonate is completely ionized into 2 $Na^{\cdot}$ and CO_3'' ions which react with OH' and H' ions of the water to form sodium hydroxide and carbonic acid respectively. The negatively charged OH' ions repel the similarly charged clay particles electrostatically. "Repulsions," he says, "may take place only when electrical charges of the particle are approximately equal. This increases the state of dispersion of the system, breaking up the larger particles into smaller ones. Hence, the water penetrates more deeply into the clay structure and causes the clay to liquify. Maximum deflocculation is brought about by a definite concentration of OH' ions and if exceeded, stiffening again takes place, the alkalinity during this period decreasing. A second liquefaction follows and is due to absorption of the salt.

J. M. Van Bemmelen, (14), says "the finely divided clay forms mole-

cular aggregates in which the added substance takes part. To do this, the solution must have a definite concentration; otherwise, too many molecular aggregates are decomposed by water and return to a finer molecular condition".

H. E. Ashley, (12), from his work with clays, has concluded that the properties exhibited by a clay-water system vary with the fineness of the particles, or in other words, the degree of dispersion is dependent upon the degree of hydrolysis of the kaolinite , either decreased or increased by the reagents added. He does not believe that the OH' ion concentration is the essential factor in effecting the deflocculation of clays. On the other hand, he claims that the alkali added to a clay reacts with its constituents and forms an alkali silicate or alumina silicate which, to some extent, is hydrolyzed so that part is present as a sol. Further alkali addition increases the amount of sodium salt in solution and in the sol state, until a point is reached where hydrolysis is set back and, consequently, diminishes the amount of sol. This continues until complete coagulation takes place.

Professor Tolman is of the opinion that an alkali added to a clay solution has its OH' ions arranged about the particles of clay in such a way that a negative surface tension is set up, causing the particles to split and remain in suspension. Coagulation of a hydroxide suspension by the addition of a salt, he explains as an electrostatic neutralization of the OH' ions by the introduction of the Na' ion, thus destroying the negative surface tension and causing the suspended particles to again grow large and settle. Coagulation by acids, he claims, is caused by a positive surface tension from the H' ions which tend to make the particles grow larger, thus decreasing the possibilities of suspension.

METHODS OF STUDY OF ADSORPTION.

VISCOSITY METHODS.

Mellor, Green, and Baugh, (15), studied the actions of acids, bases, and salts by adding varying amounts of the reagents to the clay solutions and comparing the viscosities by allowing 200 cubic centimeters of the slip to run through a modification of a Mariottes Bottle.

Bleininger, (13), has also used the viscosity method.

VOLUME MEASUREMENTS.

Patten and Gallagher, (16), have studied the effect of various salt solutions on Susquehanna clay, by shaking up 50 grams with 150 cubic centimeters of solution and allowing to settle for 7 days. The volume of solution in the soil was the basis of determinations.

Several such methods, with modifications, have been used by ceramic industries, (17).

Ashby, (18), makes measurement of the sediment after allowing a given quantity of solution to stand with a fixed amount of clay.

TITRATION METHOD.

Bleininger also used this method of determining adsorbing ability of clay. To a weighed sample of clay a constant volume of solution was added. Rapid filtering by suction, in a vessel containing air free from CO_2 was resorted to. The difference of titrations of the alkali content per cubic centimeter of the original solution and of that in the filtrate gave the amount of alkali adsorbed.

IV.

EXPERIMENTAL.

I. SUSPENSION METHOD.

The first method used was qualitative in nature and involved merely the treatment of 5 grams of clay with 98 cubic centimeters of differently concentrated acids, bases, and salts. After allowing to stand in glass stoppered graduates, the amount of suspension of the clay and the amount of sediment that existed under the varying conditions was read off and recorded.

MATERIALS.

The clay used in this study was a South Carolina Kaolin obtained from the Ceramics School. It is as nearly Al_2O_3, 2 SiO_2, $2H_2O$ as is obtainable. As taken from the bin, it was finely ground in a mortar to a fluffy powder.

The reagents used were obtained from the chemistry store rooms.

SOLUTIONS.

In these tests, the solutions were approximately .005 N,.01 N, .0133 N, .02 N of NaOH and Normal for NaCl and HCl.

II. ADSORPTION METHOD.

Most of the work was done studying the adsorbing power which clay has upon acids and alkalies and how additions of salts affected this pro-

perty. In this case 5 grams of clay were shaken vigorously with 100 cubic centimeters of solution and allowed to stand. A portion of the original solution was retained and kept under the same conditions as the clay solution, with the exception that it contained no clay. It was aimed to, in every case, titrate solutions devoid of clay particles and, in order to accomplish this, it was necessary to centrifuge alkaline clay solutions in the range of .005N---.2N concentrations.

Methyl red was used as an indicator in titrations and near the end point, all solutions were boiled to insure the absence of CO_2.

Differences in the titrations of the original solutions and those of the corresponding clay solutions gave the amount of the reagent adsorbed.

SOLUTIONS.

Solutions of HCl and NaOH were used in the titrations, the acid being standardized against Na_2CO_3 made from heating pure $NaHCO_3$ at 300 degrees C. Titration of the differently concentrated clay solutions were made with a standardized reagent of such a normality that the end point would be sharp; that is, not run over a range of so much as .1 of a cubic centimeter, and, at the same time, not be so concentrated that the addition of one drop would go past the necessary H' or OH' ions additions and thus overlap the true end point. Excluding clay solutions of .001 Normal, and of lower concentration, it was found, after a great deal of experimenting, that .1 Normal solutions seemed best adapted for the work.

APPARATUS.

The clay solutions were retained in 150 cubic centimeter glass stoppered bottles, as were the blank or original solutions.

U. S. standardized pipettes were used in drawing off set amounts of solutions for titration.

Where centrifuging was necessary to separate the clay particles from the solutions, a Sharples Centrifuge with inner bowl was used. The speed was 33,000 R. P. M.

EXPERIMENTAL RESULTS.

S U S P E N S I O N S.

SOLUTIONS	20 HOURS' STANDING	40 HOURS' STANDING	8 MONTHS' STANDING
H_2O	Turbid suspension 13 cc. Sediment	13 cc. Sediment Clear Liquid	Clear 12 cc. Sediment
.005 N. NaOH	Tan colored Suspension 5 cc. Gray colored Sediment	Tan colored Suspension 5 cc. Gray colored Sediment	89 cc. of Filmy Green White Turbidity 5 cc. Gray colored Sediment 2 Silt strata of 15.5 c.
.01 N. NaOH	Tan colored suspension 5 cc. Gray sediment	Tan colored suspension 5 cc. Gray sediment Thin tan layer on top	89 cc. of Filmy green white turbidity 5 cc. gray sediment 2 cc. of silt 5 cc. layer of brown color
.0133 N. NaOH	Tan colored suspension 5 cc. gray sediment	Tan colored suspension 4.75 cc. gray sediment	93 cc. of filmy green white turbidity 4 cc. gray sediment 1.5 cc. layer of silt
.02 N. NaOH	Tan colored suspension 6 cc. gray sediment	Tan colored suspension 5.75 cc. sediment	88 cc. of filmy green white turbidity 5.75 cc. gray sediment 1.5 cc. of light brown layer
Normal NaCl	Clear supernatant liquid 10 cc. gray sediment	Clear supernatant liquid 9.5 cc. sediment	Clear 8 cc. sediment
Normal HCl	Clear supernatant liquid 11 cc. gray sediment	Clear supernatant liquid 10 cc. sediment	Clear green supernatant liquid 8.5 cc. sediment

Further results of this nature are given in Ashley's and Bleininger's Technological papers.

ADSORPTIONS.

The adsorption of the acids and bases by clay, and the effect of salts are perhaps best shown by the curves which are to follow. In figuring adsorptions, the following formula was used.

$$\frac{N_o - N}{10 \times 5} = A.$$

Where A = Adsorptions in mols per gram of clay

N_o = Normality of the original solutions

N = Normality of solutions after adsorption.

D A T A

OF

NaOH ADSORPTION BY SOUTH CAROLINA CLAY

N_o = NORMALITY OF ORIGINAL NaOH SOLUTIONS	A = ADSORPTIONS IN MOLS PER GRAM OF CLAY.
.001	.000016
.00112	.000029
.01	.000025
.01	.000037
.0496	.000088
.05565	.0000993
.05565	.0001196
.1048	.000144
.10035	.0001392
.204	.0001234
.206	.0001489
.492	.0002176
.766	.00026
1.007	.0003084

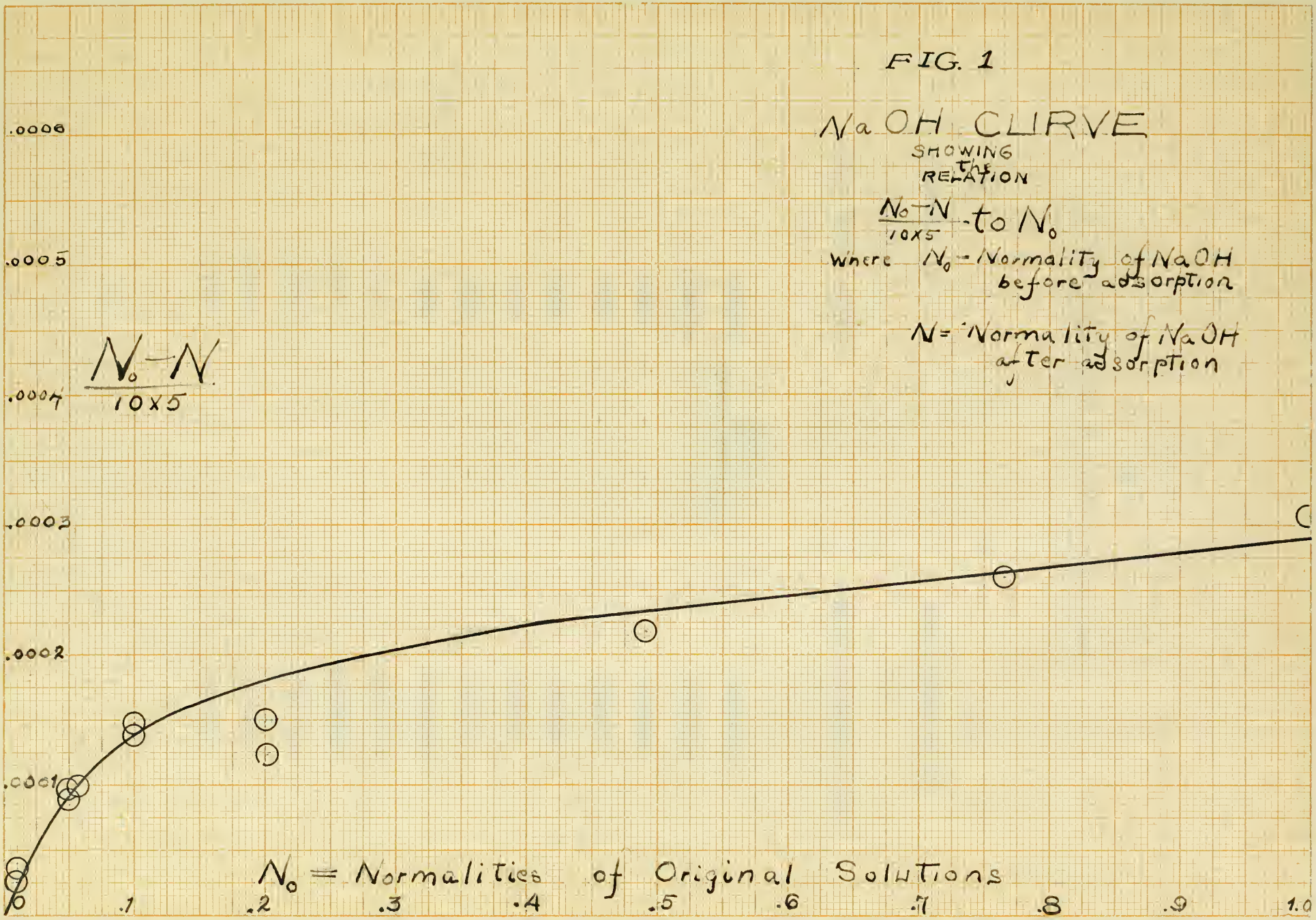


FIG. 1
NaOH CURVE
SHOWING the RELATION
$\frac{N_0 - N}{10 \times 5}$ to N_0
Where N_0 = Normality of NaOH before adsorption
N = Normality of NaOH after adsorption
$\frac{N_0 - N}{10 \times 5}$
.0006
.0005
.0004
.0003
.0002
.0001
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
N_0 = Normalities of Original Solutions

D A T A

OF

HCl ADSORPTIONS BY SOUTH CAROLINA CLAY

N_o = NORMALITY OF ORIGINAL HCl CONCENTRATIONS.	A = ADSORPTIONS OF HCl IN MOLS PER GRAM OF CLAY.
.004865	.00002196
.004988	.00002128
.00992	.0000334
.0484	.000034
.0954	.0000334
.0973	.000056
.1354	.000089
.2408	.00006832
.536	.00013664
.597	.00010249
.834	.00016708
1.024	.0002048
1.178	.0002049

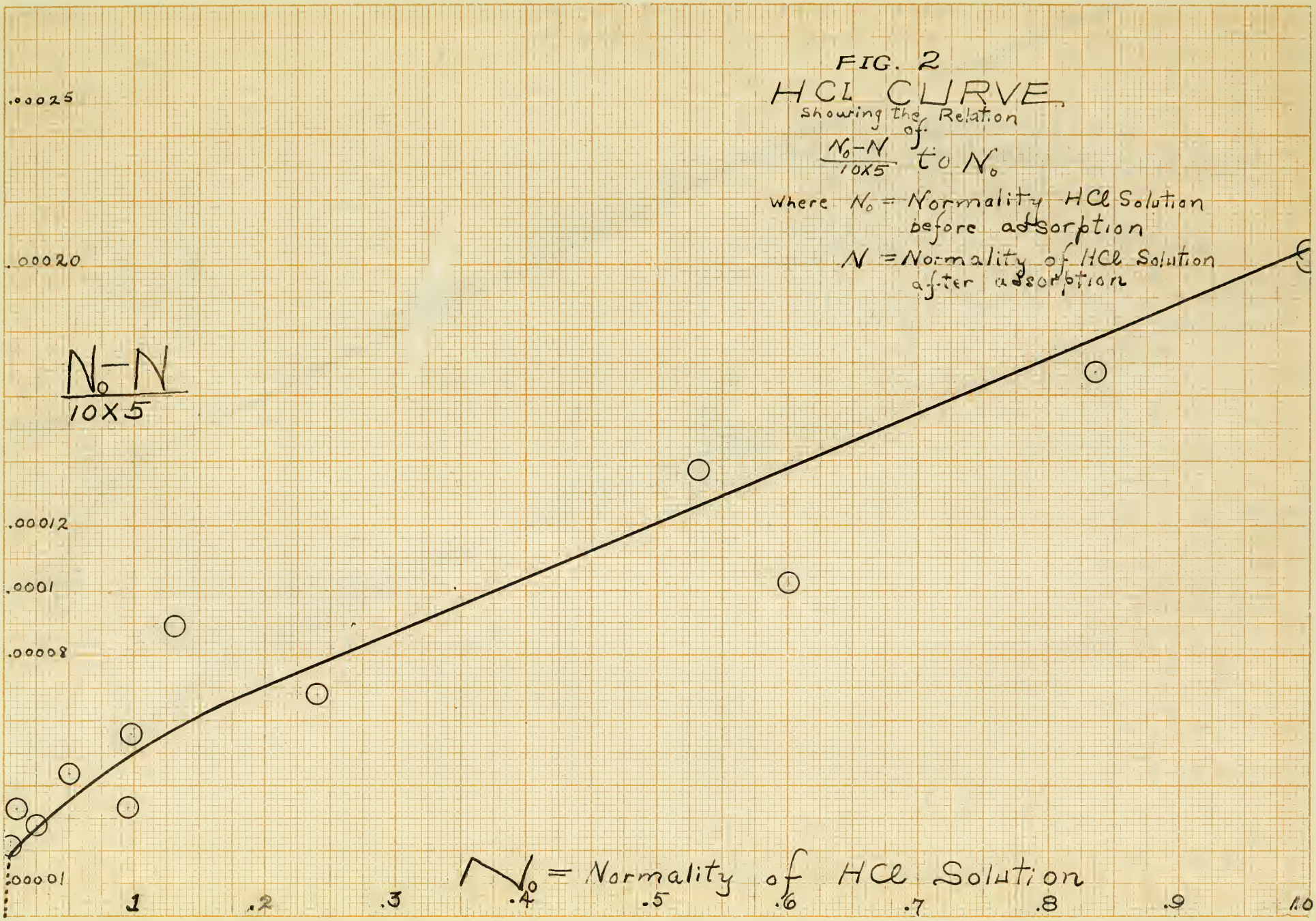


FIG. 2
HCL CURVE
Showing the Relation of
$\frac{N_0-N}{10X5}$ to N_0
Where N_0 = Normality HCl Solution before adsorption
N = Normality of HCl Solution after adsorption
$\frac{N_0-N}{10X5}$
.00025
.00020
.00012
.0001
.00008
.00001
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
N_0 = Normality of HCl Solution

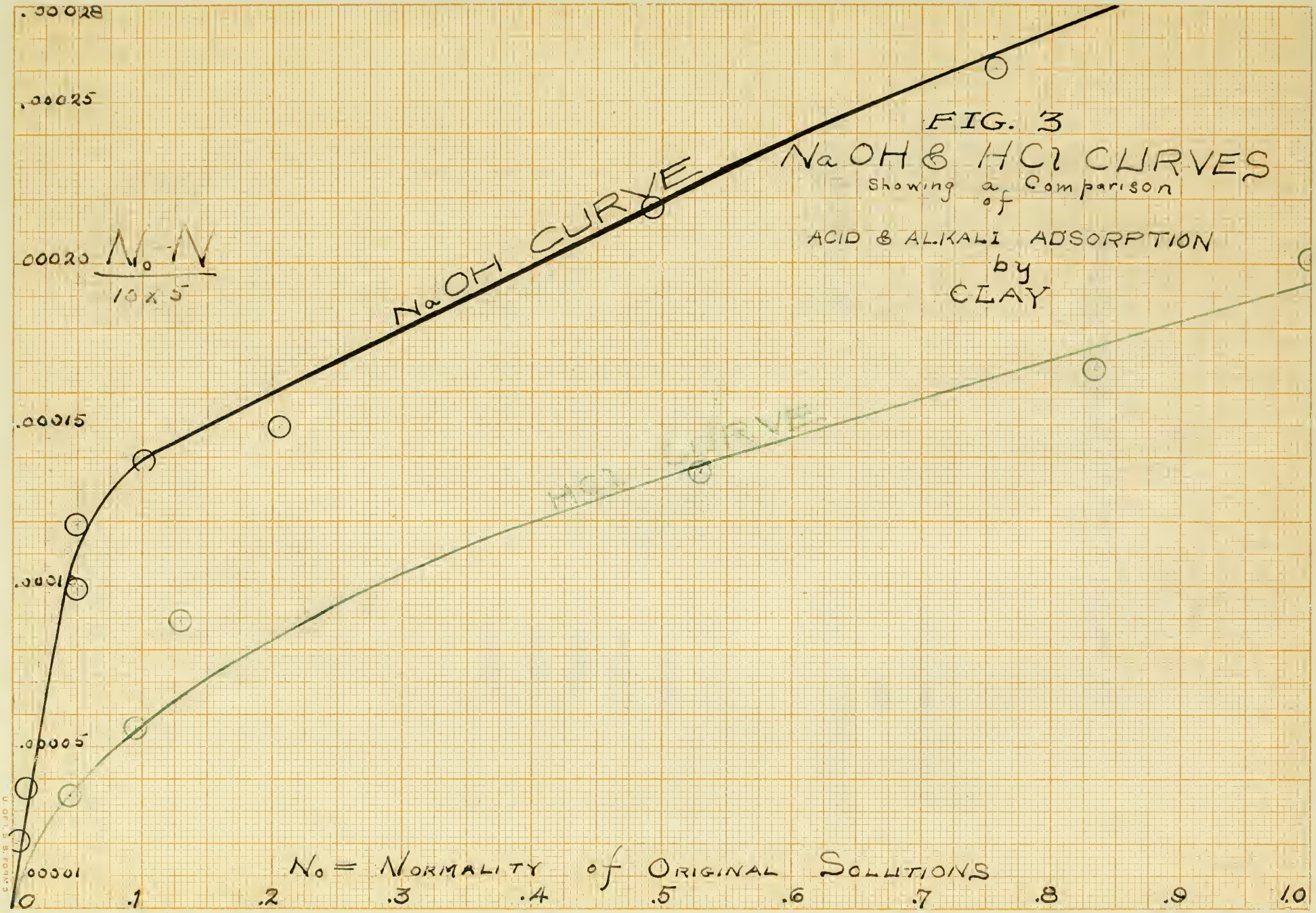


FIG. 3
NaOH & HCl CURVES
Showing a Comparison of
ACID & ALKALI ADSORPTION
by
CLAY
NaOH CURVE
HCl CURVE
$\frac{N_0 - N}{10 \times 5}$
.00028
.00025
.00020
.00015
.00010
.00005
.00001
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
N_0 = NORMALITY of ORIGINAL SOLUTIONS

D A T A

OF

NaOH ADSORPTIONS AS AFFECTED BY KCl ADDITIONS

N'_o = NORMALITY OF KCl CONCENTRATIONS.	A = ADSORPTIONS OF NaOH IN MOLS PER GRAM OF CLAY.
.01	.00011916
.05	.00013902
.1	.00012909
.3	.0013902
.5	.0001489
.9	.0001866

FIG. 4

NaOH-KCl CURVE

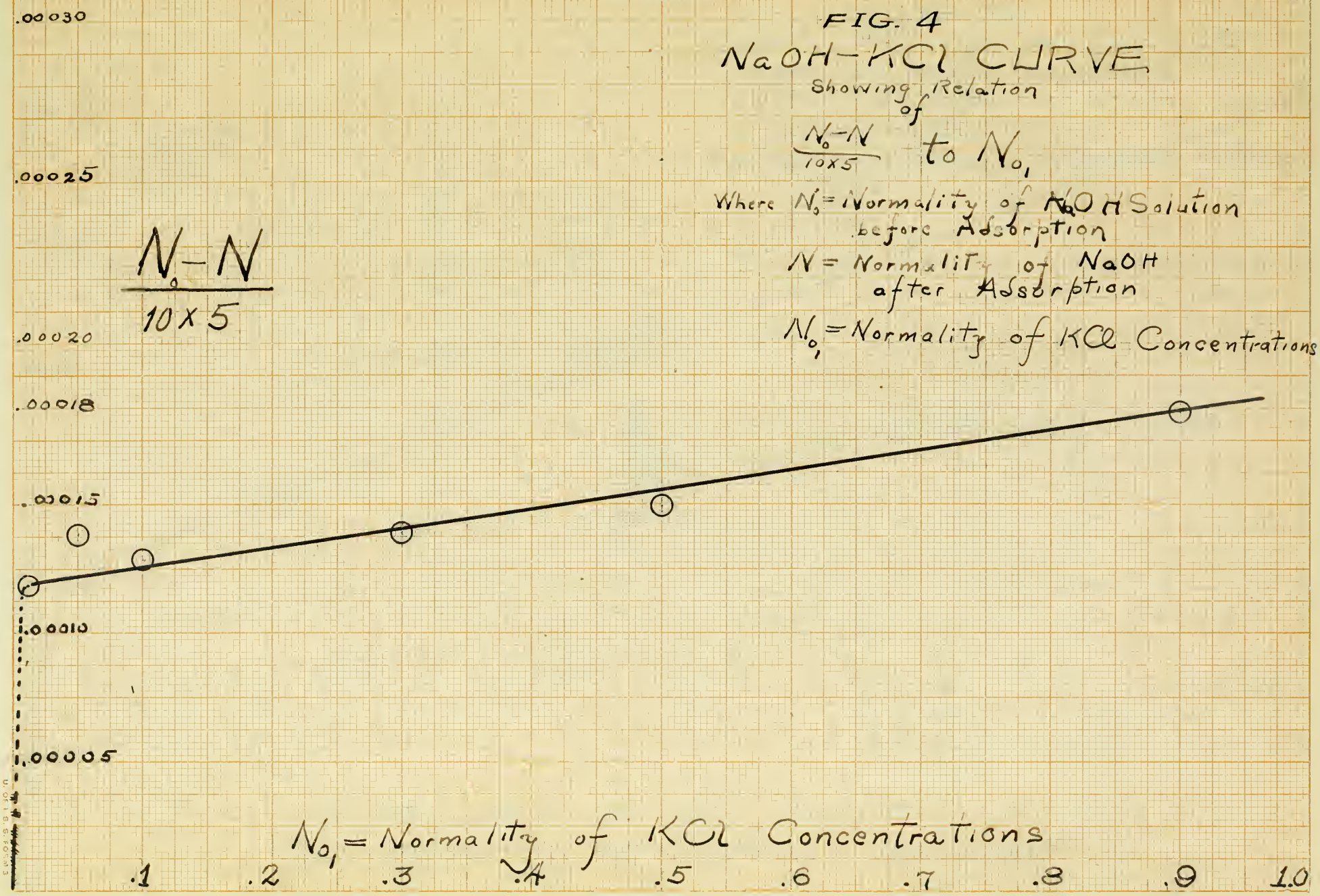
Showing Relation of

$\frac{N_0 - N}{10 \times 5}$ to N_{0_1}

Where N_0 = Normality of NaOH Solution before Adsorption

N = Normality of NaOH after Adsorption

N_{0_1} = Normality of KCl Concentrations



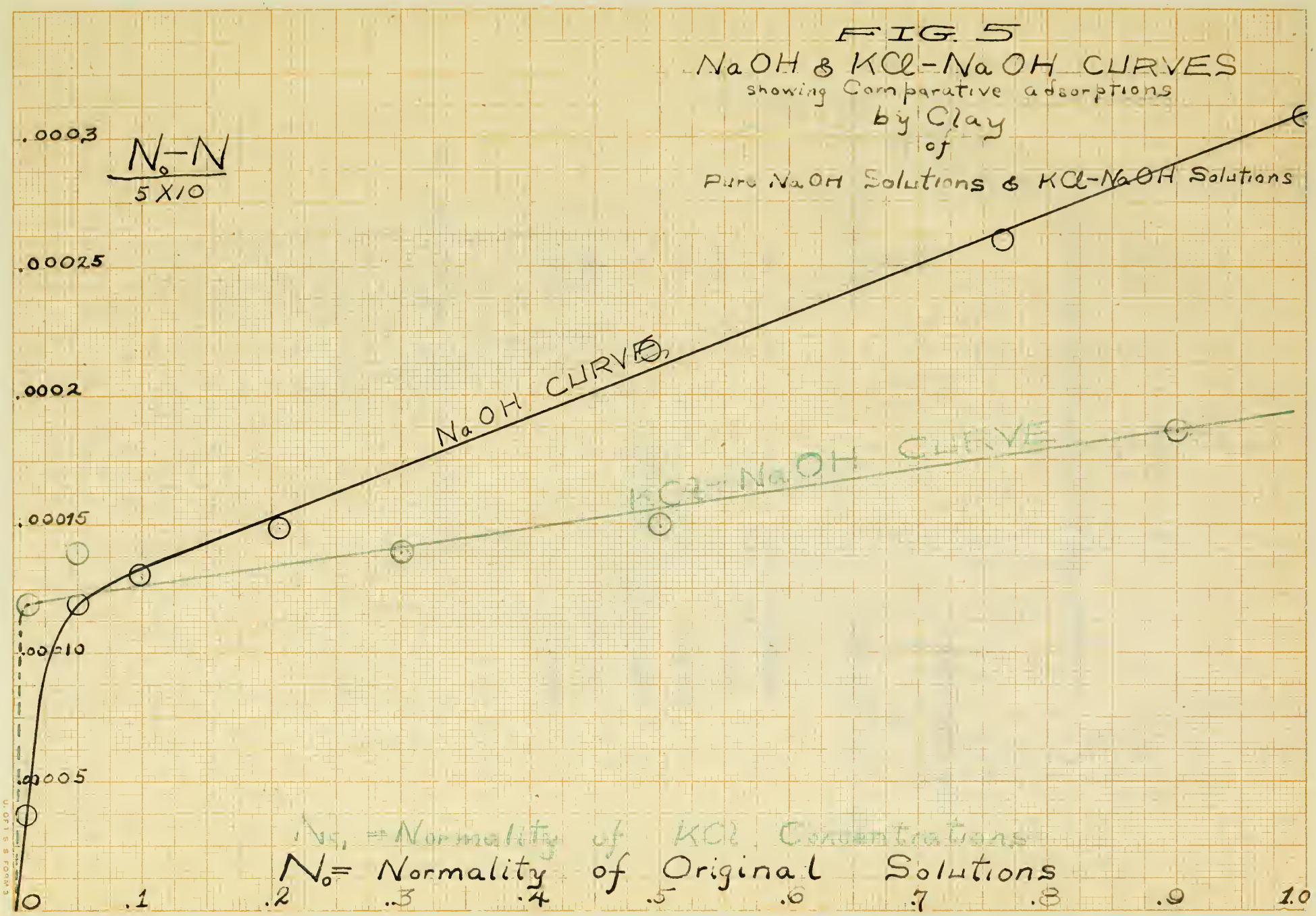


FIG. 5
NaOH & KCl-NaOH CURVES
showing Comparative adsorptions
by Clay
of
Pure NaOH Solutions & KCl-NaOH Solutions
$\frac{N_0 - N}{5 \times 10}$
.0003
.00025
.0002
.00015
.0001
.0005
0
NaOH CURVE
KCl-NaOH CURVE
N_1 = Normality of KCl Concentrations
N_0 = Normality of Original Solutions
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

D A T A

OF

HCl ADSORPTIONS AS AFFECTED BY NaCl ADDITIONS

N'_o = NORMALITY OF SALT CONCENTRATIONS.	A = ADSORPTIONS OF HCl IN MOLS PER GRAM OF CLAY.
.01 - - - - - -	.0000964
.05 - - - - - -	.0001064
.10 - - - - - -	.00011568
.30 - - - - - -	.00012532
.50 - - - - - -	.0001446
.90 - - - - - -	.00012532

HCl Normality was .1 Normal throughout.

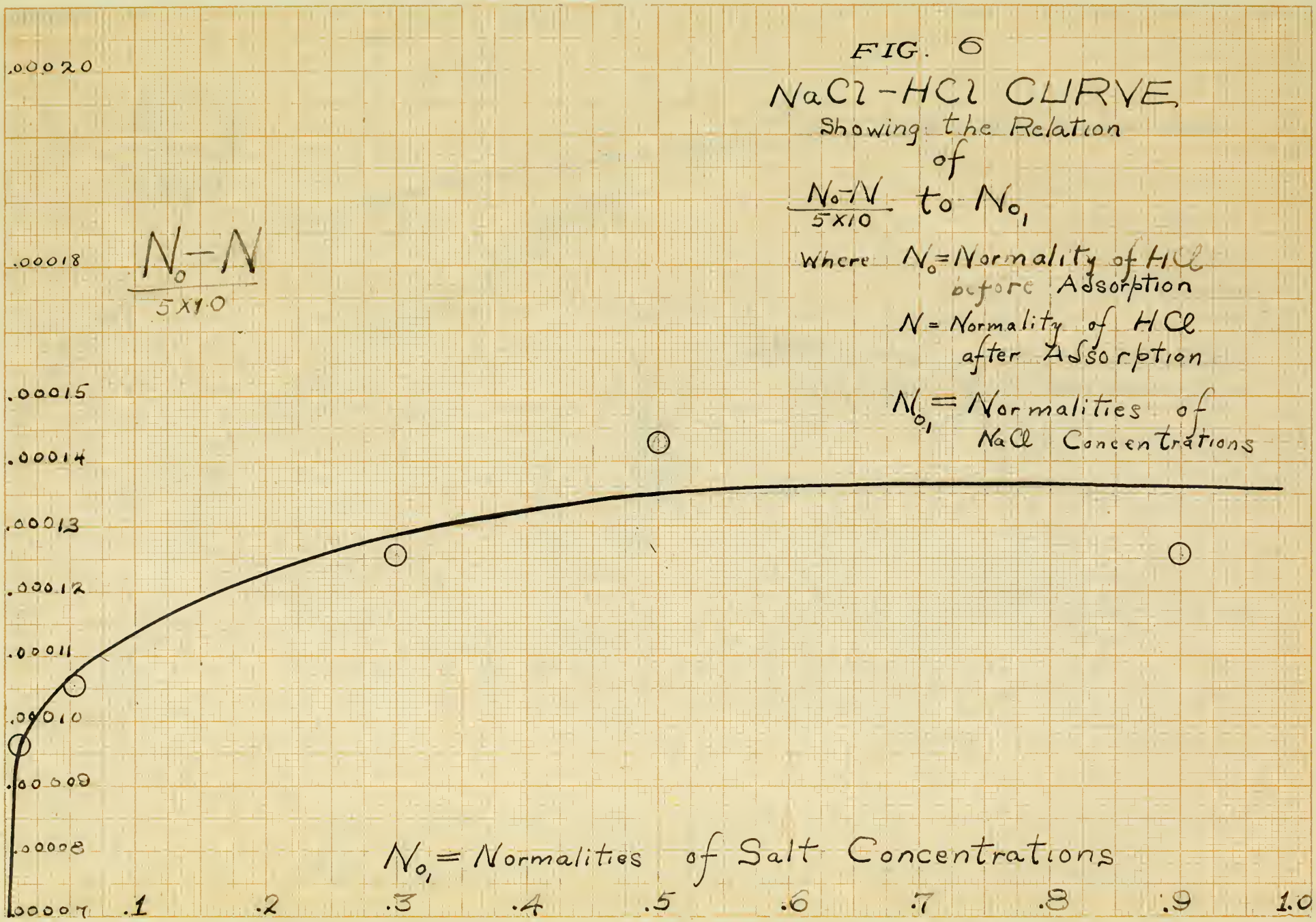


FIG. 6
NaCl-HCl CURVE
Showing the Relation of
$\frac{N_0-N}{5\times10}$ to N_{0_1}
Where N_0 = Normality of HCl before Adsorption
N = Normality of HCl after Adsorption
N_{0_1} = Normalities of NaCl Concentrations
$\frac{N_0-N}{5\times10}$
.00020
.00018
.00015
.00014
.00013
.00012
.00011
.00010
.00009
.00008
.00007
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
N_{0_1} = Normalities of Salt Concentrations

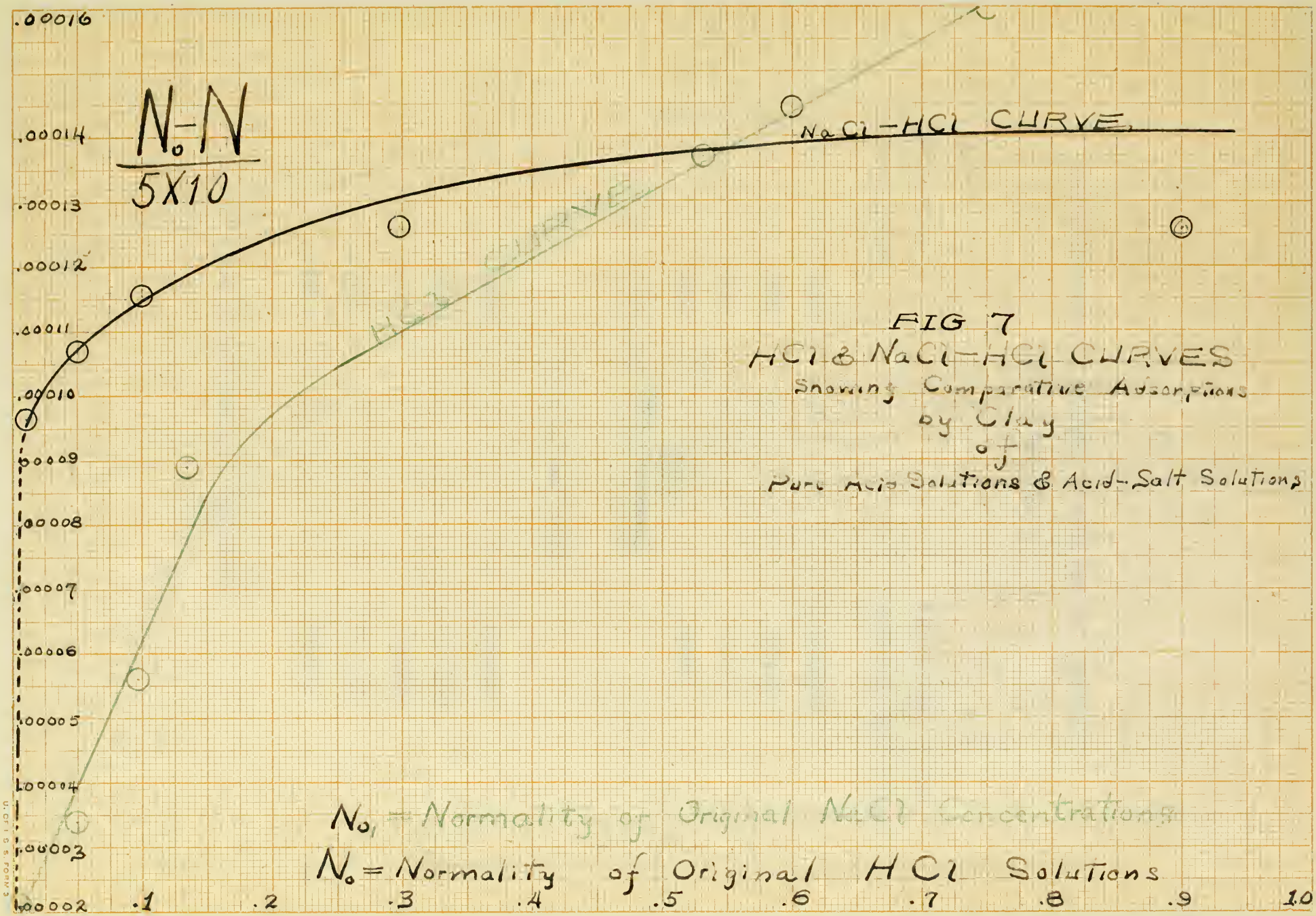


FIG 7
HCl & NaCl-HCl CURVES
Showing Comparative Adsorptions
by Clay
of
Pure Acid Solutions & Acid-Salt Solutions

D A T A

OF

NaOH ADSORPTIONS AS AFFECTED BY NaCl and KCl ADDITIONS

KCl — NaOH CURVE

N_o = NORMALITY OF NaOH SOLUTIONS.	A = ADSORPTIONS OF NaOH IN MOLS PER GRAM OF CLAY.
.05135	.00003972
.1503	.00010923
.3924	.0001728
.865	.000243

1 gr. of NaCl was used throughout.

NaCl — NaOH CURVE

.00845	.0000636
.04465	.00013902
.1433	.00015888
.3952	.0001688
.868	.0002920

.772 gr. of NaCl was used throughout.

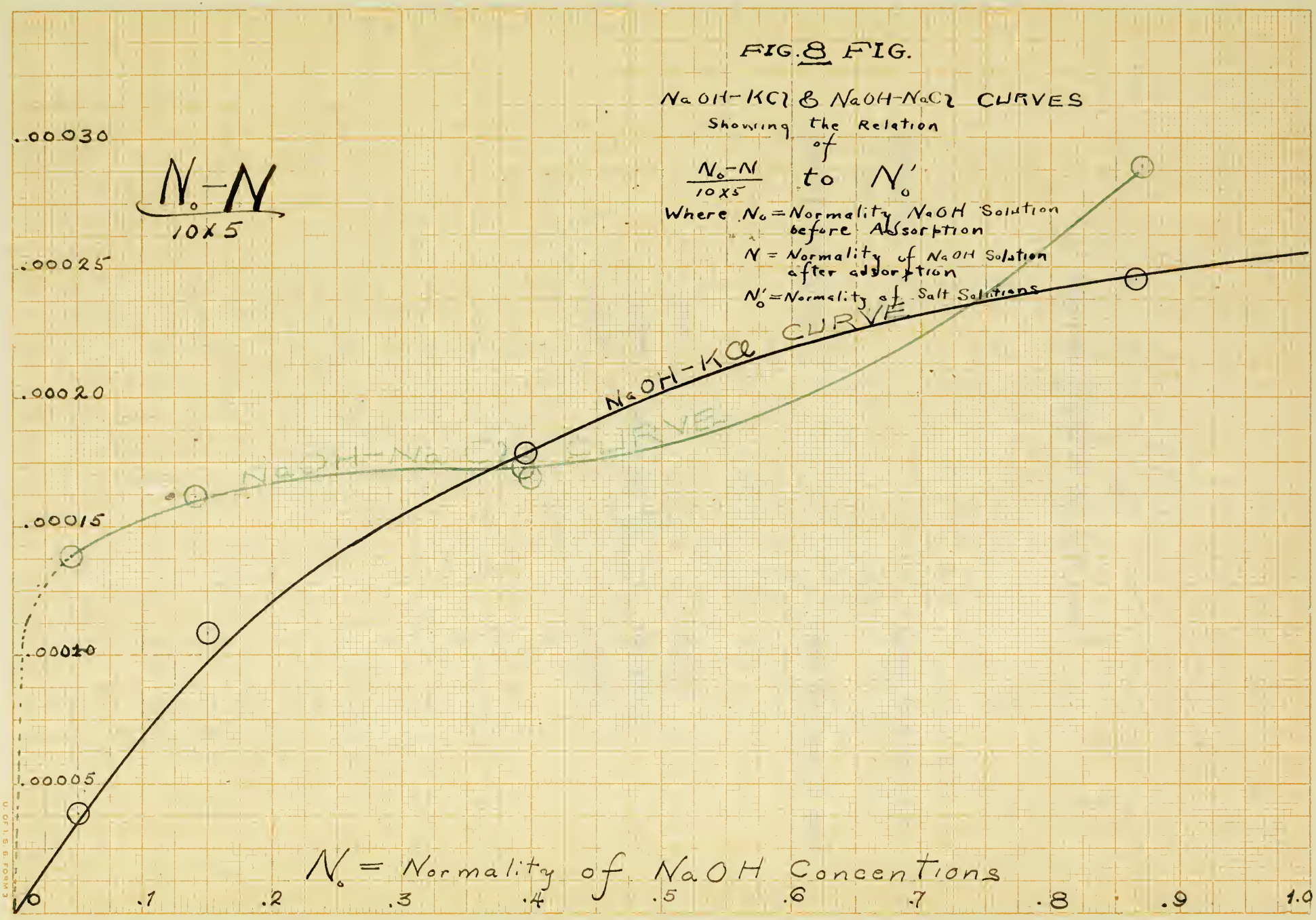


FIG. 8 FIG.
NaOH-KCl & NaOH-NaCl CURVES
Showing the Relation of
$\frac{N_0-N}{10\times5}$ to N_0'
Where N_0 = Normality NaOH Solution before Absorption
N = Normality of NaOH Solution after absorption
N_0' = Normality of Salt Solutions
$\frac{N_0-N}{10\times5}$
.00030
.00025
.00020
.00015
.00010
.00005
NaOH-KCl CURVE
NaOH-NaCl CURVE
N_0 = Normality of NaOH Concentrations
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

D A T A

OF

NaOH ADSORPTIONS BY PURIFIED CLAY

N_0 = NORMALITY OF ORIGINAL SOLUTIONS.	A = ADSORPTIONS OF NaOH IN MOLS PER GRAM OF CLAY.
.0105	.000108
.10277	.00020852
.4923	.0003808

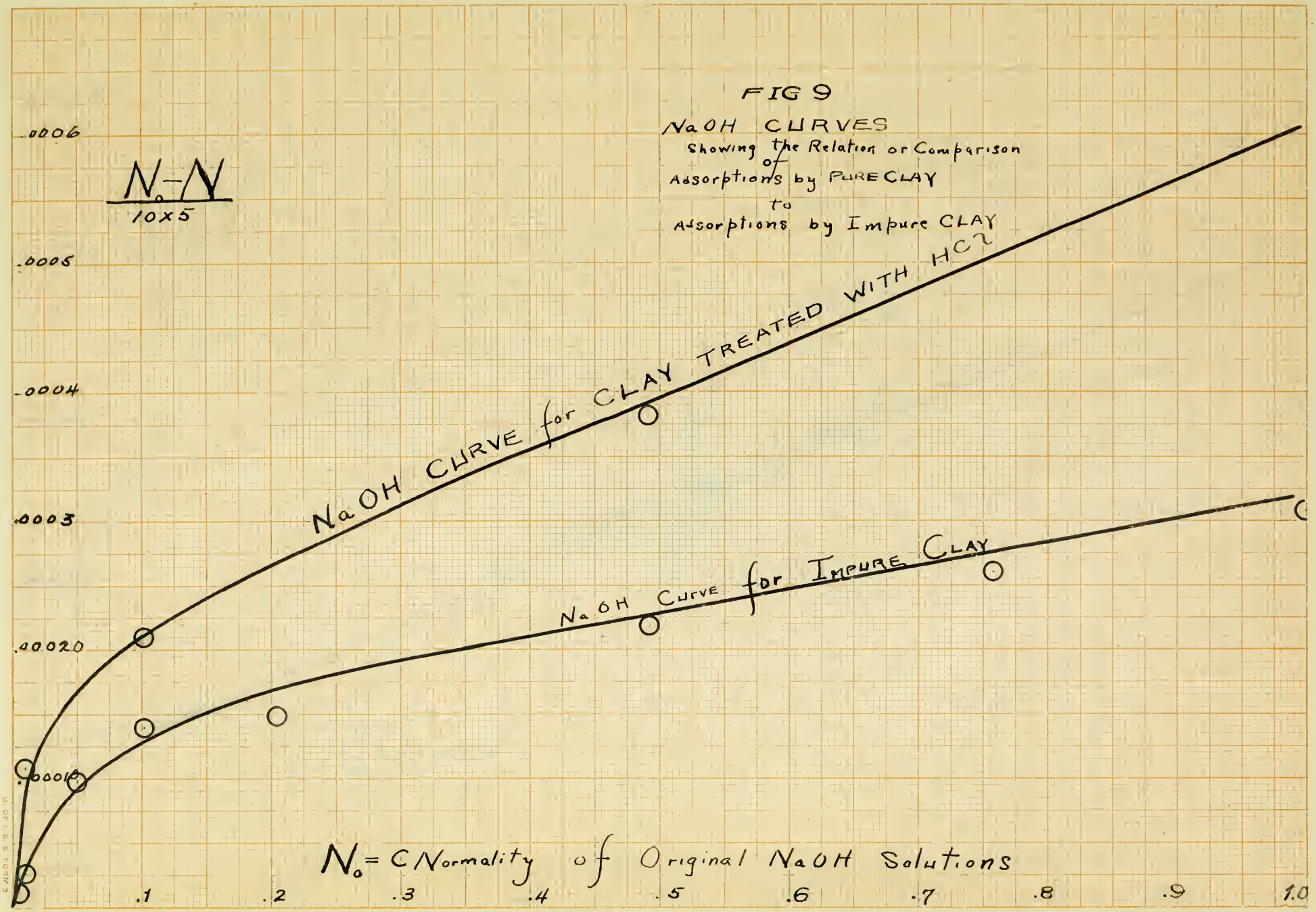


FIG 9
NaOH CURVES
Showing the Relation or Comparison of Adsorptions by PURE CLAY to Adsorptions by Impure CLAY
$\frac{N_0 - N}{10 \times 5}$
.0006
.0005
.0004
.0003
.00020
.00010
NaOH CURVE for CLAY TREATED WITH HCl
NaOH Curve for IMPURE CLAY
N_0 = C Normality of Original NaOH Solutions
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

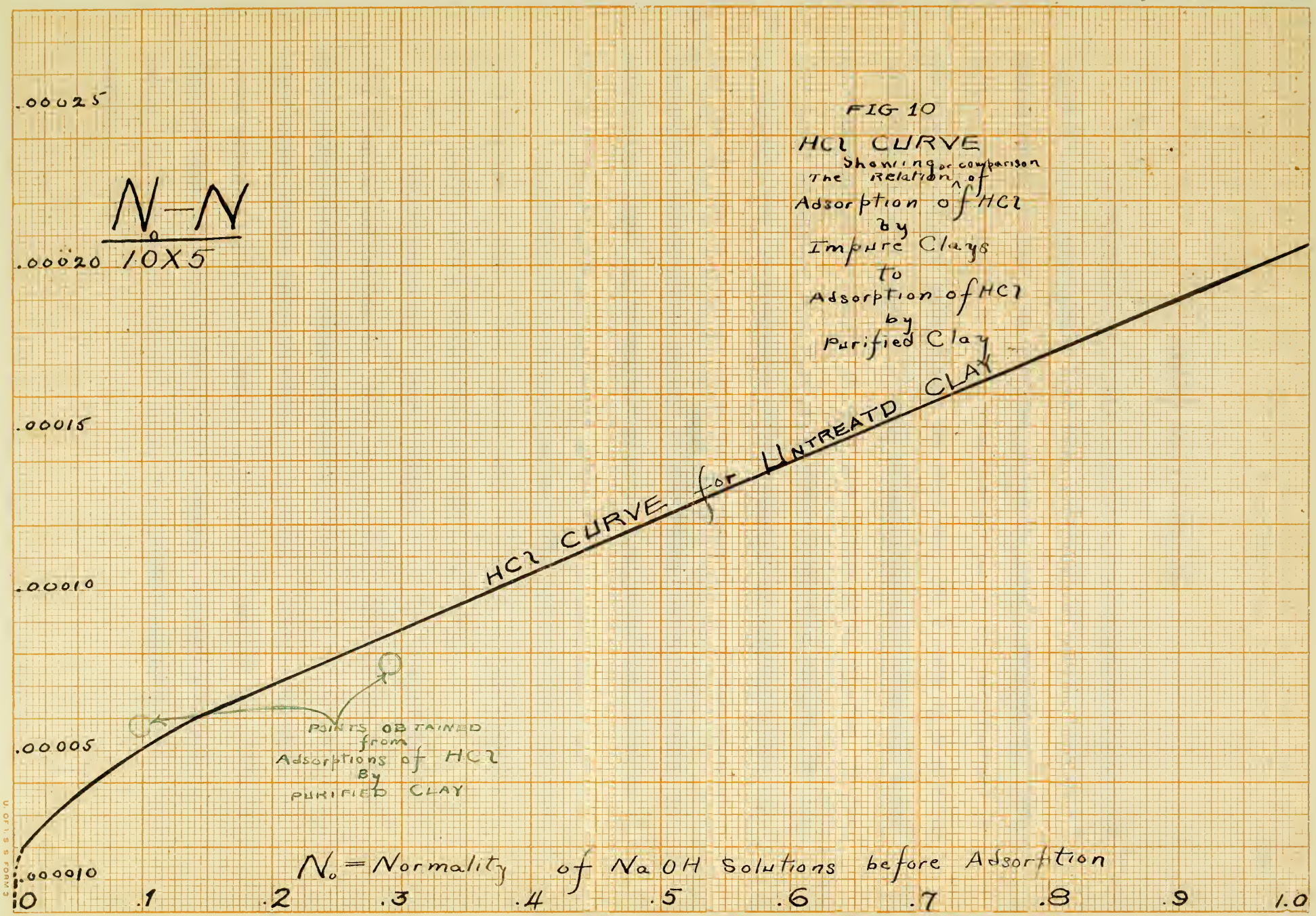


FIG 10
HCl CURVE
Showing for comparison
The Relation of
Adsorption of HCl
by
Impure Clays
to
Adsorption of HCl
by
Purified Clay
$\frac{N_0 - N}{10 \times 5}$
.00025
.00020
.00015
.00010
.00005
.000010
HCl CURVE for UNTREATD CLAY
POINTS OBTAINED
from
Adsorptions of HCl
By
PURIFIED CLAY
N_0 = Normality of NaOH Solutions before Adsorption
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

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SUMMARY AND CONCLUSIONS.

The table on suspensions shows that the buoying up of particles may exist for a surprisingly long time, providing, of course, that an approximately correct concentration of the OH' ions is maintained. Observations seem to show that this concentration lies in the neighborhood of .01 N and is further borne out by the fact that .01 N NaOH is a solution from which it is extremely difficult to centrifuge clay particles, while concentrations on both sides of .01 N give little or no trouble. So far, this leads to nothing of a convincing nature other than that the OH' ion is necessary for the attainment of the phenomena of suspension, but whether the OH' ion is a direct cause for it (that is, if it accords with Bleininger's electrostatic theory) or whether it effects it through indirect means (that is, by reaction with the clay to form colloidal hydrates of Al, Si, etc.,) is another question.

The effect of salts upon the absorbing power of clay, as shown by the curves in Figs. 5 and 7 would tend to support an electrostatic theory, or the surface tension theory of Prof. Tolman's.

Further support of these theories was given by experiments with clay freed of its impurities. That is, to purify, the clay was treated with concentrated HCl, bringing into solution all free Fe, Al, and Si that might under certain conditions exist as colloids; and by subsequent repeated washings these free elements together with the acid were eliminated from the clay. Tests with the purified material revealed adsorptions as before, and in case of NaOH solutions, even greater adsorptions were recorded.

Clay particles, then, do not depend upon their coatings of colloidal materials for the phenomena of suspension. The hydroxyl ion either causes dispersion by its electrostatic effect or it reacts with the clay and forms new colloidal substances, which in turn go into suspension.

Should the NaOH do the latter, some OH' ions would be retained in solution as colloidal $Al(OH)_3$, $Fe(OH)_3$, and $Si(OH)_3$ and not in the clay itself. Consequently, the clay when separated from the solution would not carry with it as great a concentration of OH' ions as it would were there no colloids to keep the OH' ions back; so that upon titrating the differences between N_0 and N would not be as great. This would tend to indicate that when a clay solution is free of colloidal substances, there should be a greater difference between N_0 and N. Indeed, this assumption is well borne out by adsorptions shown by curves in Fig. 9.

In considering these phenomena, then, it is necessary to fall back to some electrostatic theory. Whether the suspension is due to the Brownian movement or is a question of surface tension remains for the ultramicroscope and the ingenious brain to solve.

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